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Ab initio and kinetic Monte Carlo study of lithium diffusion in LiSi, $Li_{12}Si_7$, $Li_{13}Si_5$ and $Li_{15}Si_4$

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HIGHLIGHTS

- Li ion migration dynamics in the Li–Si alloys are investigated from DFT calculation.
- Identification of vacancy mechanism as dominant mode of diffusion in Li-Si compounds.
- Li ions diffuse predominantly via a vacancy–mediated mechanism in Li_xSi ($1 < x$).
- Li migration barriers in Li_xSi (~0.37 eV) and its migration pathways are discussed.
- Macroscopic Li diffusion coefficients in Li_xSi are predicted using KMC simulation.

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ABSTRACT

The kinetics of lithium atoms in various Li–Si binary compounds are investigated using density functional theory calculations and kinetic Monte Carlo calculations. The values of the Li migration energy barriers are identified by NEB calculations with vacancy–mediated, interstitial and exchange migration mechanisms in crystalline LiSi, $Li_{12}Si_7$, $Li_{13}Si_4$, and $Li_{15}Si_4$. A comparison of these NEB results shows that the vacancy–mediated Li migration is identified as the dominant diffusion mechanisms in Li–Si compounds. The diffusion coefficients of Li in Li–Si compounds at room temperature are determined by KMC simulation. From the KMC results, the recalculated migration energy barriers in LiSi, $Li_{12}Si_7$, $Li_{13}Si_4$, and $Li_{15}Si_4$ correspond to 0.306, 0.301, 0.367 and 0.320 eV, respectively. Compared to the Li migration energy barrier of 0.6 eV in crystalline Si, the drastic reduction in the Li migration energy barriers in the lithiated silicon indicates that the initial lithiation of the Si anode is the rate-limiting step. Furthermore, it is also found that Si migration is possible in Li–rich configurations. On the basis of these findings, the underlying mechanisms of kinetics on the atomic scale details are elucidated.

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1. Introduction

Increasing demand of high energy density lithium ion batteries (LIBs) for large scale energy storage and for application in electric vehicles has stimulated intensive search on the high capacity electrodes over the past decades [1–3]. Among suitable high-capacity alternatives to commercial carbonaceous anode materials, silicon is considered as a promising anode material for LIBs due to a large theoretical capacity (4200 mAh g^{-1}) which is an order of magnitude greater than that of graphite (372 mAh g^{-1}) [4–6]. However, its benefit in applications requiring high capacity storage is limited by the drastic volumetric deformation during charge/discharge cycles and subsequent mechanical failure [7–9]. Averting the electrochemical–mechanical degradation remains one of the major challenges in the development of high capacity Si anode materials [10,11].

The cycle performance of Si anode has been greatly improved over recent years by adopting the nanoengineering of Si [12–14].

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Although these approaches can radically improve the capacity, rate and cyclability of Si based electrodes, the intrinsic drawbacks, such as stress generation and fracture that lead to capacity fading, cannot be overcome due to a lack of critical knowledge on the fundamental dynamic lithiation mechanisms.

Recent studies of lithiated silicon have revealed the stress generation induced by non-uniformly distributed lithium concentration, leading to several studies into the diffusion induced stress in Si anodes [15−22]. The study of lithiation dynamics becomes more crucial for Si anodes. Many papers available in literature focused on the lithiation process of bulk Si using atomic scale analysis, such as molecular dynamics simulation and density functional theory calculation [23−25]. Their simulations revealed that the lithiation/delithiation process is strongly facet dependent for crystalline Si, although Li migration is isotropic in bulk Si [23−25]. The insights gained could therefore help in developing strategies to mitigate mechanical failure during the anisotropic morphological changes and the microstructural evolutions of Si nanostructures. On the other hand, the lithium ion migration dynamics in lithiated Si is another important kinetics problem, which is strongly associated with the rate performance of the anode material and the diffusion induced stress on lithiated state. Although Li ion diffusion behavior in both crystalline and amorphous Si has been intensively studied both by theoretical and experimental approaches, little information concerning Li ion diffusion behavior is available for the Li−Si alloy phase [26−28]. Furthermore, the Li−Si phases dominate the lithiation/delithiation process of the Si anode and the phase transition processes between various Li−Si alloys are controlled by the Li diffusivity within the Li−Si phases and at the interface region [29,30].

Experimental studies [31−35] and theoretical analyses [36,37] of Li diffusivity in Li_xSi ($x > 1$) show a discrepancy in the reported values of the Li diffusivity for $x > 1$, with diffusivities spanning 2−3 orders of magnitude: $D_{Li} \approx 10^{-11}–10^{-8}\ \mathrm{cm^2\ s^{-1}}$ at room temperature. Recently, Shenoy et al. performed ab-initio molecular dynamics (MD) simulations to observe Li migration in a Li_1Si medium in liquid phase and calculated D_{Li} in Li-Si phase by extrapolation method from liquid to solid phase [36]. Qu et al. developed a modified embedded-atom method (MEAM) potential for the Li-Si binary system in liquid phase to calculate D_{Li} using classical MD simulations [37]. Their extrapolation techniques from the liquid to the solid phase predicted different values for the Li diffusivity [36,37]. Li diffusion is inherently atomistic and long simulation times are required to describe the macroscopic motion of Li atoms using MD. Although these advanced computational studies produced a precise understanding of the Li kinetic behavior in liquid Li−Si systems, these attempts to extrapolate into solid phase are still far from being quantitative and are not capable of determining the details of Li kinetic behavior in solid state Li−Si systems. The atomistic diffusion mechanism in liquid phase and solid phase of Li-Si systems may be qualitatively different and the extrapolation may not be a reasonable approximation. Recently, Yao et al. also reported Li migration energy barriers using ab-initio calculation [38,39]. Nevertheless, it is not currently understood how the Li migration barriers of diverse diffusion mechanisms would determine the diffusivity of Li_xSi ($x = 1$–4) in solid phases.

In this study, we focus on Li kinetics in Li_xSi ($x > 1$) using density functional theory (DFT) calculations. Our calculated results provide an atomic level description of Li diffusion mechanisms and quantitative migration energy barriers of Li in various phases of c−Li_xSi compounds. The results shows that the Li diffusivity values in Li−Si systems are highly dependent on Li concentration. Moreover, the homogeneous macroscopic diffusion in Li_xSi phases are gained by using a kinetic Monte Carlo simulation (KMC) to cover large time scales.

2. Computational methods

Ab-initio calculations were performed using the DFT method with local density approximation (LDA) [40]. We used the projector augmented wave (PAW) method with a plane wave basis set as implemented in the Vienna ab-initio simulation package (VASP) [41]. For Li atoms, the Li−sv pseudo−potential treated the semi−core 1s states as valence states for an accurate description of Li^+ ionic states. The energy cutoff for the plane wave basis set was 500 eV. A k−point sampling mesh in the Monkhorst−Pack scheme was set to $7 \times 7 \times 7$ (for LiSi) and $5 \times 5 \times 5$ (for $Li_{15}Si_4$, $Li_{13}Si_4$, and $Li_{12}Si_7$) for the Li_xSi compounds. All atoms were fully relaxed using the conjugate gradient method until the residual forces on the constituent atoms decreased below 0.01 eV $Å^{-1}$ for geometry optimization: cell parameters, volume cells, and atomic positions. To study the kinetic behavior of Li in Li_xSi, migration energy barriers were calculated using the climbing−image nudged elastic band (NEB) method on predicted diffusion pathways. The macroscopic Li diffusion coefficient in Si and Li_xSi was obtained using the KMC simulations. The KMC technique, based on the DFT energy barrier results, attempted to capture the effects of atomic kinetic processes that directly contribute to changes in macroscopic properties. The results from the KMC simulations were statistically averaged over 10 samples.

The detailed KMC algorithm for simulating the time evolution was described in our previous publications [28,42,43]. The outline of the processes is: (i) Identify all possible events from current atomic configurations. In this study, we considered first nearest neighbor (<3.5 Å) Li sites from sites of Li vacancy defects. (ii) Determine a list of the rates (k_i) of all possible transition events in the system. The rates are proportional to $v \times \exp(-E_m/kT)$, where the migration energy barrier (E_m) was obtained from the ab-initio calculations and the attempt frequency (v) was calculated by using the vibration frequency ratio between initial and saddle points. (iii) Calculate a cumulative function $K_i = \sum_{j=1}^{i} k_j$ for $i = 1, \ldots, N$ at each current vacancy position. (iv) Generate a pseudorandom number u between 0 and 1. (v) Advance the statistical time of each step (Δt) by $-\ln(u)/K_N$. (vi) Find one event to carry out i by finding the i for which $K_{i-1} < uK < K_i$. (vii) Reconfigure the system according to the chosen event. (viii) Update new position of the Li atoms and simulation time. (ix) Return to step (i). The diffusion coefficient of Li is

$$D = \lim_{t \to \infty} \frac{\langle r^2 \rangle}{6t} \tag{1}$$

where t is the time calculated as the sum of all the Δt of each jump and $\langle r^2 \rangle$ is the mean-squared displacement.

3. Results of DFT and KMC calculations

For the DFT simulation of Li diffusivity in Li−Si systems, we calculate the Li migration energy barriers of the Li-Si compounds shown in Fig. 1. The migration energy barriers in LiSi and $Li_{15}Si_4$ are calculated by using three diffusion mechanisms (interstitial, exchange and vacancy) as initial and final phases of Li_xSi compounds, respectively. We also check the Li migration energy barriers in the $Li_{12}Si_7$ and $Li_{13}Si_4$ using only vacancy−mediated mechanism. The detailed motion dynamics in $Li_{12}Si_7$ are compared with experimental data [35].

To describe the Li diffusivity in a macroscopic point of view, KMC simulations are performed at various temperatures. The calculated Li diffusion coefficients in Li_xSi compounds are compared with Huggins' work at 700 K [34]. Our study on c−Li_xSi can also provide insights into the kinetic behavior of Li in a−Li_xSi since the complex

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